

## PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION  
(PCT Rule 61.2)

To:

Assistant Commissioner for Patents  
 United States Patent and Trademark  
 Office  
 Box PCT  
 Washington, D.C.20231  
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year)
20 June 2000 (20.06.00)

International application No.	Applicant's or agent's file reference
PCT/GB99/03619	256

International filing date (day/month/year)	Priority date (day/month/year)
02 November 1999 (02.11.99)	02 November 1998 (02.11.98)

Applicant
KATHIRGAMANATHAN, Poopathy

1. The designated Office is hereby notified of its election made:

in the demand filed with the International Preliminary Examining Authority on:

27 May 2000 (27.05.00)

in a notice effecting later election filed with the International Bureau on:

\_\_\_\_\_

2. The election  was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  S. Mafia
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# PARENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>256</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, Item 5 below.	
International application No. <b>PCT/GB 99/ 03619</b>	International filing date (day/month/year) <b>02/11/1999</b>	(Earliest) Priority Date (day/month/year) <b>02/11/1998</b>
Applicant <b>SOUTH BANK UNIVERSITY ENTERPRISES LTD. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of **4** sheets.

It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

a. With regard to the language, the International search was carried out on the basis of the International application in the language in which it was filed, unless otherwise indicated under this item.

the International search was carried out on the basis of a translation of the International application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the International application, the International search was carried out on the basis of the sequence listing :

contained in the International application in written form.

filed together with the International application in computer readable form.

furnished subsequently to this Authority in written form.

furnished subsequently to this Authority in computer readable form.

the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the International application as filed has been furnished.

the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2.  Certain claims were found unsearchable (See Box I).

3.  Unity of invention is lacking (see Box II).

### 4. With regard to the title,

the text is approved as submitted by the applicant.

the text has been established by this Authority to read as follows:

**ELECTROLUMINESCENT MATERIALS**

### 5. With regard to the abstract,

the text is approved as submitted by the applicant.

the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International search report, submit comments to this Authority.

### 6. The figure of the drawings to be published with the abstract is Figure No. \_\_\_\_\_

as suggested by the applicant.

because the applicant failed to suggest a figure.

because this figure better characterizes the invention.

None of the figures.

## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

## (PCT Article 36 and Rule 70)

Applicant's or agent's file reference 256	<b>FOR FURTHER ACTION</b>		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB99/03619	International filing date (day/month/year) 02/11/1999	Priority date (day/month/year) 02/11/1998	
International Patent Classification (IPC) or national classification and IPC C09K11/06			
Applicant SOUTH BANK UNIVERSITY ENTERPRISES LTD. et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 8 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I  Basis of the report
- II  Priority
- III  Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV  Lack of unity of invention
- V  Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI  Certain documents cited
- VII  Certain defects in the international application
- VIII  Certain observations on the international application

Date of submission of the demand 27/05/2000	Date of completion of this report 12.03.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Shade, M Telephone No. +31 70 340 2332



INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

International application No. PCT/GB99/03619

I. Basis of the report

1. This report has been drawn on the basis of (substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):  
**Description, pages:**

1-9 as originally filed

**Claims, No.:**

1-25 as originally filed

**Drawings, sheets:**

1/6-6/6 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB99/03619

the drawings,      sheets:

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims 6, 7, 12, 13, 14, 17, 20, 21, 24
	No:	Claims 1-5, 8, 9, 10, 11, 15, 16, 18, 19, 22, 23, 25
Inventive step (IS)	Yes:	Claims 6
	No:	Claims 1-5, 7-25
Industrial applicability (IA)	Yes:	Claims 1-25
	No:	Claims

2. Citations and explanations  
**see separate sheet**

**VII. Certain defects in the international application**

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/03619

**1) R Item V**

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

**1.1) Reference is made to the following documents:**

- D1: Kidorui (1995), 26, 110-11
- D2: Japanese Journal Of Applied Physics. Tokyo (01-04-1993), 32(4A, PART 02), L511-L513
- D3: Aust. J. Chem. (1994), 47(2), 365-84
- D4: US-A-5757026
- D5: Kidorui (1991), 18, 70-1
- D6: US-A-5128587
- D7: US-A-5755999
- D8: WO-A-9802018
- D9: Science, (03-03-1995), 267(5202), 1332-1334

**1.2) Claims 1-5, 7-25 do not satisfy the criteria of Article 33(2) and (3) PCT.**

- 1.3) Document D1 discloses an electroluminescent device comprising a Mg:Ag cathode, an aluminium trisquinoline electron-transporting layer, an emitting layer comprising the bluish green emitting  $Tb(acac)_3(Phen)$  (regarding the colour of emitted light see paragraph 3.5 below), or an emitting layer comprising a mixture of this complex and a europium complex, a TPD hole-transporting layer and an ITO coated glass substrate, thereby disclosing the subject-matter of present claims 1, 2, 8, 9, 10, 11, 15, 16, 18, 19, 22, 23, 25.**
- 1.4) Dependent claims 7, 12, 13, 14, 17, 20, 21 and 24 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty or inventive step, the reasons being as follows:**
  - i) regarding claim 7 the use of polymeric matrices in the active layers of electroluminescent devices is well established in the art, see D8, page 27, lines 4**

to 15.

ii) regarding claims 12, 13 and 14 emitting layers comprising a mixture of hole-transporting and light-emitting materials are well known in the art, see D8, Example 1. The particular hole-transporting molecules of present claims 13 and 14 are those most commonly used in the art, see D8, page 23, line 30 to page 27, line 2 and D1, Figure 1.

iii) regarding claim 17, electroluminescent devices in which the emitting layer comprises a mixture of electron-transporting and light-emitting materials are well known in the art, see D6, Example 8.

iv) regarding claims 20 and 21 the addition of fluorescent dyes to the emitting layer of electroluminescent devices to modify the colour of light emitted is well known in the art, see D7, column 7, lines 31 to 48.

v) regarding claim 24 electroluminescent devices in which there are a plurality of layers of electroluminescent material are well known in the art, see D9, Figure 1.

- 1.4) D2 discloses a number of photoluminescent zinc complexes which emit in the blue or purplish blue spectrum, according to the CIE 1931 chromacity diagram, and their use in electroluminescent devices, these devices comprise a MgIn cathode, an emitting layer of the zinc complex, a TPD hole-transporting layer and an ITO anode, see D2, Table I and page L512, column 1, second paragraph. D2 thereby discloses the subject-matter of present claims 1, 8, 9, 10, 11, 15, 22, 23.
- 1.5) D3 discloses the complexes Gd(terpyridine)Cl<sub>3</sub> and Y(terpyridine)Cl<sub>3</sub>, see D3 page 367 and 368, structures numbered (vi) and (xv). These complexes correspond to examples 2 and 4 of the present application. D3 discloses the subject-matter of present claims 1 to 5.
- 1.6) D4 discloses the compound scandium (4-methoxy-picolylmethylketone) bis(acetylacetone) which is described as having photoluminescence of 433nm, which is in the purple region according to the CIE 1931 chromacity diagram. D4 discloses the subject-matter of present claims 1 and 2.

- 1.7) D5 discloses a complex of europium and 15-crown-5 type ligands, the complex has blue photoluminescence. D5 discloses the subject-matter of present claims 1, 3 and 4.
- 1.8) The subject-matter of present claim 6 satisfies the criteria of Article 33(1), (2) and (3) PCT because such a molecule is not disclosed in or rendered obvious by the prior art.
- 1.9) The subject-matter of present claims 1-25 satisfy the criteria of Article 33(4) PCT having industrial application in the field of electroluminescent devices.

**2) Re Item VII**

Certain defects in the international application

- 2.1) Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1 to D9 is not mentioned in the description, nor are these documents identified therein.

**3) Re Item VIII**

Certain observations on the international application

- 3.1) Independent claims 1 and 2 and their dependent claims 3 to 5 and 7 to 25 do not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The claims attempt to define the subject-matter in terms of the result to be achieved which merely amounts to a statement of the underlying problem, i.e. the claims attempt to define a class of complexes in terms of the colour of light which they emit when in fact the problem to be solved is to provide a class of compounds emitting light in these ranges.
- 3.2) Claim 1 refers to an organic complex of a transition metal emitting in the blue or purplish blue spectrum, the description supplies only a single embodiment in which a transition metal is used, in this case a yttrium complex emitting greenish blue light. Claim 1 is therefore not supported by the description as required by Article 6 PCT, as its scope is broader than justified by the description.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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3.3) The embodiment of the invention described on page 2, lines 16 to 20 does not fall within the scope of the claims. This embodiment refers to the proposed invention as providing an electroluminescent compound which comprises an organic complex of a transition metal, whereas claim 2, the only independent claim to refer to electroluminescent compounds, only mentions organic complexes of lanthanides and actinides. This inconsistency between the claims and the description leads to doubt concerning the matter for which protection is sought, thereby rendering the claims unclear (Article 6 PCT).

3.4) A number of the claims contain features which are not referred to in the description and are therefore not supported by the description, as required by Article 6 PCT. The claims concerned are as follows:

- i) claim 15, there is no support in the description for an electroluminescent device in which there is a metal anode in direct contact with the electroluminescent material.
- ii) claims 18 and 19 in so far as they refer to electroluminescent devices comprising oxadiazoles, there is no support in the description for an electroluminescent device having an electron injecting material comprising an oxadiazole.
- iii) claim 24, there is no support in the description for an electroluminescent device in which there are a plurality of layers of electroluminescent material.
- iv) claim 25, there is no support in the description for an electroluminescent device in which the electroluminescent material is formed of two or more different electroluminescent compounds.

3.5) The embodiments of the invention described as examples 2 and 3 do not fall within the scope of the claims. Since claim 1 only refers to photoluminescent compounds emitting light in the blue or purplish blue spectrum whereas example 2 has greenish blue photoluminescence and example 3 has white photoluminescence. This inconsistency between the claims and the description leads to doubt concerning the matter for which protection is sought, thereby

rendering the claims unclear (Article 6 PCT). This lack of clarity leads to the conclusion that the term blue in claims 1 and 2 should be interpreted in its broadest sense, with the result that the complexes and devices of D1, which emit bluish green light, must be considered to fall within the scope of independent claims 1 and 2 and the dependent claims outlined in paragraph 1.3 above.

- 3.6) The dependency of claims 12 to 14 on claim 8 and the dependency of claim 16 on claim 15 renders their subject-matter and that of the claims as a whole unclear. Claim 8 refers to an electroluminescent compound being deposited on a transparent substrate and claim 15 refers to a metal anode in contact with an electroluminescent material. Contrary to these limitations claims 12 to 14 and claim 16 then describe other layers as being inserted between the electroluminescent layer and the layer it is deposited on/in contact with. This is contrary to the requirement of Rule 6.4(a) and (b) PCT and gives rise to a lack of clarity of the claims as a whole, Article 6 PCT.
- 3.7) The dependency of claim 12 on claim 11 renders the subject-matter of said claims and the claims as a whole unclear contrary to Article 6 PCT. Claim 12 refers to an electroluminescent device comprising a mixture of hole-transporting material and electroluminescent material in the emitting-layer, it is dependent on claim 11 which refers to an electroluminescent device having separate hole-transporting and emitting layers. It is not clear whether the device of claim 12 comprises both a hole-transporting layer and a layer containing a mixture of light-emitting compound and hole-transporting compound or a single layer comprising a mixture of light-emitting compound and hole-transporting compound.
- 3.8) The unit torr employed in on page 8 is not additionally expressed in terms of the units stipulated by Rule 10.1(a) PCT.
- 3.9) Since it is clear from D1 and D2 that blue electroluminescence has been produced in the prior art the statement on page 2, lines 29 and 30 that "hitherto it has not been possible to produce blue light by means of electroluminescence" gives rise to a lack of clarity of the claims when interpreted in the light of the description, Article 6 PCT.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> :  C09K 11/06, H05B 33/14, H01L 51/20		A1	(11) International Publication Number: <b>WO 00/26323</b>  (43) International Publication Date: 11 May 2000 (11.05.00)
<p>(21) International Application Number: PCT/GB99/03619</p> <p>(22) International Filing Date: 2 November 1999 (02.11.99)</p> <p>(30) Priority Data: 9823761.3 2 November 1998 (02.11.98) GB</p> <p>(71) Applicant (for all designated States except US): SOUTH BANK UNIVERSITY ENTERPRISES LTD. [GB/GB]; 103 Borough Road, London SE1 0AA (GB).</p> <p>(72) Inventor; and</p> <p>(75) Inventor/Applicant (for US only): KATHIRGAMANATHAN, Poopathy [GB/GB]; 14 Sandhurst Avenue, North Harrow, Middlesex HA2 7AP (GB).</p> <p>(74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Westerham, Kent TN16 2BB (GB).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b>  <i>With international search report.  Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: ELECTROLUMINESCENT MATERIALS</p> <p>(57) Abstract</p> <p>A novel electroluminescent compound which emits blue or blueish purple light is a complex of a lanthanide or actinide and an organic complex e.g. mono(bathophenanthroline) thoriumIV chloride or mono(triptyridyl)yttrium chloride.</p>			

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## ELECTROLUMINESCENT MATERIALS

5 The present invention relates to electroluminescent materials and to devices incorporating them.

Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications. Liquid crystal devices and devices which are based on inorganic semiconductor systems are widely used, 10 however these suffer from the disadvantages of high energy consumption, high cost of manufacture, low quantum- efficiency and the inability to make flat panel displays, reflectance problems, i.e. low visibility in bright conditions and a narrow viewing angle e.g. +/- 45°.

15 Organic polymers have been proposed as useful in electroluminescent devices, but it is not possible to obtain pure colours, they are expensive to make and have a relatively low efficiency.

20 Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

25 In an article in Chemistry letters pp 657-660, 1990 Kido et al disclosed that a terbium (III) acetyl acetonate complex was green electroluminescent and in an article in Applied Physics letters 65 (17) 24 October 1994 Kido et al disclosed that a europium (III) triphenylene diamine complexes was red electroluminescent but these were unstable in atmospheric conditions and difficult to produce as films.

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The complexes disclosed in these articles had a relatively low photoluminescent efficiency and were only able to produce green or red light and other colours could not be produced.

5 We have now discovered photoluminescent and electroluminescent compounds and materials which emit blue and purplish blue light.

According to the invention there is provided an photoluminescent compound which comprises an organic complex of a transition metal, lanthanide or an actinide and an 10 organic ligand which photoluminescent compound emits light in the blue or purplish blue spectrum.

It has surprisingly been found that it is possible by choice of the metal and the organic ligand to form a complex which, when an electric current is applied across it will 15 emit blue or purplish blue light.

The invention also provides an electroluminescent compound which comprises an organic complex of a transition metal, a lanthanide or an actinide and an organic ligand which electroluminescent compound emits light in the blue or purplish blue 20 spectrum when an electric current is passed through it.

The colour of light is subjective and colours can be defined by co-ordinates on a two dimensional chart in which colours are areas on the chart and in the present invention the blue and purplish blue spectrum is defined as the area bounded by the co-ordinates in the colour chart CIE 1931 a copy of which is shown in Fig. 1. The 25 complexes of the invention enable light within the co-ordinates (0, 0) (0, 0.3) (0.3, 0) to be produced.

Light in the blue region of the spectrum is difficult to produce and hitherto it has not 30 been possible to produce blue light by means of electroluminescence.

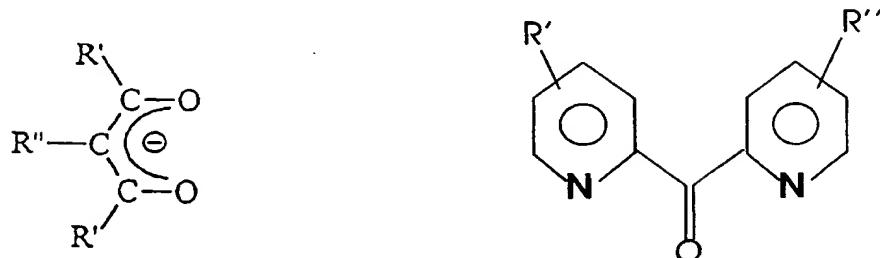
- 3 -

The preferred metals are thorium (IV), yttrium (III), gadolinium (III), europium (II), terbium(IV), cerium(IV) and cerium (III). A mixture of metals can be used to form mixed chelates.

5

The preferred ligands are

10



or

15 where R' is the same or different at different parts of the molecule and each R'' and R' is a substituted or unsubstituted aromatic or heterocyclic ring structure or a hydrocarbyl or a fluorocarbon or R'' is fluorine or hydrogen or R'' is copolymerised with a monomer e.g. or R' is t-butyl and R'' hydrogen.

20 Preferably each of R', R'', and R' is an alkyl group preferably a -C(CH<sub>3</sub>) group,

Preferred complexes are TMHD (Tris(2,2,6,6-tetramethyl-3,5-heptanedionato),  $\alpha'$ ,  $\alpha''$ ,  $\alpha'''$  tripyridyl, bathophen (4,7-diphenyl-1,1-phenanthroline), crown ethers and cryptans.

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Particularly preferred complexes are the thorium bathophen, yttrium tripyridyl and TMHD, and europium TMHD complexes.

5 A novel complex with strong photoluminescent and electroluminescent properties is Eu(II)(TMHD)<sub>2</sub> complex which is stable in air. It would have been expected that such a Eu(II) complex would have been unstable in the presence of oxygen and it is surprising that this complex is air stable.

10 The complexes of the present invention can be used to form electroluminescent devices.

15 The electroluminescent devices of the invention comprise a transparent substrate which is a conductive glass or plastic material which acts as the anode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate. The electroluminescent material can be deposited on the substrate directly by evaporation from a solution of the material in an organic solvent. The solvent which is used will depend on the material for example alcohols such as ethanol, 20 ketones such as acetone and methyl acetylacetone, and chlorinated hydrocarbons such as dichloromethane are suitable in many cases.

25 Alternatively the material can be deposited by spin coating or by vacuum deposition from the solid state e.g. by sputtering or any other conventional method can be used.

In one embodiment of the invention there is a hole transporting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transporting layer. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without

- 5 -

recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

Hole transporting layers are used in polymer electroluminescent devices and any of

5 the known hole transporting materials in film form can be used.

The hole transporting layer can be made of a film of an aromatic amine complex such as poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl)-1,1'-biphenyl -4,4'-diamine (TPD), polyaniline etc.

10

Optionally dyes such as fluorescent laser dyes, luminescent laser dyes etc. can be included to modify the colour spectrum of the emitted light.

Preferably the electroluminescent material is mixed with an inert polymeric material

15

such as a polyolefin e.g. polyethylene, polypropylene etc. and preferably polystyrene.

Preferred amounts of the electroluminescent material in the mixture is from 95% to 5% by weight of active material and more preferably 25 to 20% by weight.

The hole transporting compound can optionally be mixed with the electroluminescent

20

material in a ratio of 5-95% of the electroluminescent material to 95 to 5% of the hole transporting compound. In another embodiment of the invention there is a layer of an electron injecting material between the cathode and the electroluminescent material

layer, this electron injecting material is preferably a metal complex such as a metal quinolate e.g. an aluminium quinolate which will transport electrons when an electric current is passed through it. Alternatively the electron injecting material can be

25 mixed with the electroluminescent material and co-deposited with it.

In a preferred structure there is a substrate formed of a transparent conductive

30 material which is the anode on which is successively deposited a hole transportation

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layer, the electroluminescent material layer and an electron injection layer which is connected to the anode. The anode can be any low work function metal e.g. aluminium, calcium, lithium, silver/magnesium alloys etc.,

5

The preparation of compounds of the invention are shown in the examples

Example 1

10

Mono(bathophenanthroline)thorium(IV)chloride. Thorium(IV)chloride (5 mmol, 1.87 g) was dissolved in ethanol/water mixture (2:1 v/v) (75 ml) at 50°C. Bathophenanthroline (5 mmol, 1.66 g) was dissolved in a mixture of ethanol/dichloromethane (2:1 v/v) (75 ml) and added portionwise to the solution of the thorium salt. The mixture was reduced on a hotplate at 100°C over one hour. The precipitate was filtered to give an off-white solid which was washed with diethylether (2 x 25 ml) and dried in vacuo to yield the product (1.9 g).

Example 2

20

Mono( $\alpha'$ ,  $\alpha''$ ,  $\alpha'''$ tripypyridyl)yttrium(III) chloride. Yttrium(III) chloride (2 mmol, 0.61 g) was dissolved in ethanol (100 ml) and  $\alpha'$ ,  $\alpha''$ ,  $\alpha'''$  tripyridyl (2 mmol, 0.47 g) was added. The reaction mixture was warmed for 60 minutes at 50°C and the solvents removed. The residue was washed with diethylether (2x25 ml) and dried in vacuo to give the product (0.80g).

Example 3

- 7 -

Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium(III) mono( $\alpha'$ , $\alpha''$ , $\alpha'''$  tripyridyl). The tris-chelate (1 mmol, 0.64 g) was dissolved in ethanol (100 ml) and  $\alpha'$ ,  $\alpha''$ ,  $\alpha'''$  tripyridyl (1 mmol, 0.23 g) was added. The reaction mixture was warmed for 60 minutes at 50°C and the solvents removed. The residue was washed with 5 diethylether (2x25 ml) and dried in vacuo to give the product (0.50 g). Yield 57%.

#### Example 4

Mono( $\alpha'$ ,  $\alpha''$ ,  $\alpha'''$  tripyridyl)gadolinium(III) chloride. Gadolinium(III) chloride 10 (0.37 g, 1 mmol) was dissolved in ethanol (150 ml) and  $\alpha'$ ,  $\alpha''$ ,  $\alpha'''$ -tripyridyl (0.23 g, 1 mmol) was added. The reaction mixture was heated under reflux for 1 hour and the solvent removed in vacuo to give the gadolinium adduct (Yield 0.50 g).

#### Example 5

15 Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(II). The reaction was carried out under anhydrous conditions using dried glassware under dry nitrogen and using acetyl nitrile freshly distilled over phosphorus pentoxide. Europium(II) chloride (1.0 g, 5 mmol) was placed in a 250 ml three-neck round-bottom flask fitted with a 20 condenser, two dropping funnels and nitrogen bubbler. Deoxygenated solution of the diketone (1.84 gms 10 mmol) in acetyl nitrile (50 ml) was placed in the first dropping funnel and deoxygenated acetyl nitrile (150 ml) was placed in the second dropping funnel. Both funnels were under nitrogen and fitted with nitrogen balloons. Acetyl nitrile was allowed to run into the flask and the mixture stirred at 50°C (oil bath) until 25 dissolution. The diketone solution was then added to the flask and the reaction mixture refluxed for one hour and allowed to cool under nitrogen overnight. The dry diethylether and dried in vacuo at 60°C. (Yield 0.82 g). The filtrate was dried to give pale yellow tris(2,2,6,6-tetramethyl-3,5-heptaneionato)europium(II). (Yield 0.90 g).

Electroluminescent devices were fabricated and tested.

### I. Device Fabrication

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An ITO coated glass piece ( $1 \times 1\text{cm}^2$  cut from large sheets purchased from Balzers. Switzerland) had a portion etched out with concentrated hydrochloric acid to remove the ITO and was cleaned and placed on a spin coater (CPS 10 BM, Semitec. Germany) and spun at 2000 rpm for 30 seconds, during which time the solution of the 10 electroluminescent compound was dropped onto it dropwise by a pipette.

Alternatively the electroluminescent compound was vacuum evaporated onto the ITO coated glass piece by placing the substrate in a vacuum coater and evaporating the electroluminescent compound at  $10^{-5}$  to  $10^{-6}$  torr onto the substrate.

15

The organic coating on the portion which had been etched with, the concentrated hydrochloric acid was wiped with a cotton bud.

20

The coated electrodes were stored in a vacuum desiccator over calcium sulphate until they were loaded into a vacuum coater (Edwards,  $10^{-6}$  torr) and aluminium top contacts made. The active area of the LED's was  $0.08\text{ cm}^2$  by  $0.1\text{ cm}^2$  the devices were then kept in a vacuum desiccator until the electroluminescence studies were performed.

25

The ITO electrode was always connected to the positive terminal. The current vs. voltage studies were carried out on a computer controlled Keithly 2400 source meter.

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Electroluminescence spectra were recorded by means of a computer controlled charge coupled device on Insta Spec photodiode array system model 77II2 (Oriel Co.. Surrey, England)

5

## 2. Photoluminescence Measurements

Photoluminescence was excited using 325nm line of Liconix 4207 NB, He/Cd laser. The laser power incident at the sample ( $0.3\text{mWcm}^{-2}$ ) was measured by a Liconix 55PM laser power meter. The radiance calibration was carried out using Bentham radiance standard (Bentham SRS8, Lamp current 4,000A, calibrated by National Physical laboratories, England. The PL studies were carried out on samples or films. The Complexes of the examples were tested and the results shown in the Table and the Spectra attached as Figs. 2 to 6

10  
15

Table

Example	PL %	$\lambda_{\text{max}}/\text{nm}$	CIE		Colour
			x	y	
1	1.0	450	0.17	0.15	Purple
2	6.0	410,520	0.21	0.32	Greenish Blue
3	0.03	460	0.21	0.29	White
4	16	320,450			Purple
5	0.9	420	0.18	0.05	Purple

- 10 -

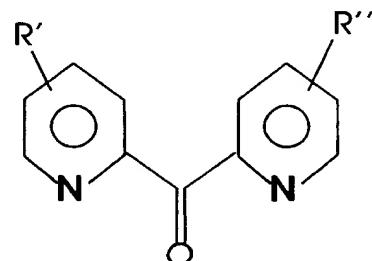
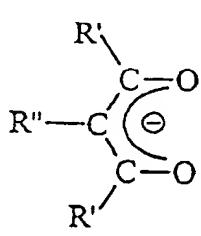
Claims

5 1. A photoluminescent compound which comprises an organic complex of a transition metal, a lanthanide or an actinide and an organic ligand which photoluminescent compound emits light in the blue or purplish blue spectrum.

10 2. An electroluminescent compound which comprises an organic complex of a lanthanide or an actinide and an organic ligand which electroluminescent compound emits light in the blue or purplish blue spectrum when an electric current is passed through it.

15 3. A compound as claimed in claim 1 or 2 which comprises a complex of thorium (IV), yttrium (III), gadolinium (III), europium (II), terbium(IV), cerium(IV) and cerium (III) or a mixture of one or more of these.

4. A compound as claimed in claim 1, 2 or 3 in which the ligand is selected from



20 or

where R' maybe the same or different at different parts of the molecule and each of R'' and R' is a substituted or unsubstituted aromatic or heterocyclic ring structure or a hydrocarbyl or a fluorocarbon or R'' is fluorine or hydrogen or R'' is copolymerised 25 with a monomer or is an alkyl group preferably a -C(CH<sub>3</sub>) group, or is selected from

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TMHD,  $\alpha$ ,  $\alpha'$ ,  $\alpha''$ ,  $\alpha'''$  tripyridyl, bathophen (4,7-diphenyl-1,10-phenanthroline), crown ethers and cryptans.

5. A compound as claimed in claim 4 in which the ligand is selected from thorium (IV) bathophen, yttrium (III) tripyridyl and yttrium (III) TMHD, and europium (II) TMHD complexes.
6. Eu(II)(TMHD)<sub>2</sub>.
- 10 7. A composition which comprises an inert polymer and from 5% to 95% by weight of an electroluminescent compound as claimed in any one of the preceding claims.
- 15 8. An electroluminescent device which comprises a transparent substrate on which is deposited an electroluminescent compound as claimed in any one of the preceding claims.
9. An electroluminescent device as claimed in claim 8 in which the transparent substrate comprises a conductive glass or plastic material which acts as the anode.
- 20 10. An electroluminescent device as claimed in claim 9 in which the transparent substrate comprises an indium tin oxide coated glass.
- 25 11. An electroluminescent device as claimed in any one of claims 8 to 10 in which there is a hole transporting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transporting layer.
- 30 12. An electroluminescent device as claimed in claim 11 in which there is a hole transporting material mixed with the electroluminescent material in a ratio of 5 to 95% of the electroluminescent material to 95 to 5% of the hole transporting compound.

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13. An electroluminescent device as claimed in claim 12 in which the hole transporting layer is an aromatic amine complex.
- 5 14. An electroluminescent device as claimed in claim 13 in which the hole transporting layer is poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl)-1,1'-biphenyl -4,4'-diamine (TPD) or polyaniline.
- 10 15. An electroluminescent device as claimed in any one of claims 8 to 14 in which there is a metal anode in contact with the electroluminescent material.
16. An electroluminescent device as claimed in any one of claims 8 to 15 in which there is a layer of an electron injecting material between the cathode and the electroluminescent material layer
- 15 17. An electroluminescent device as claimed in any one of claims 8 to 16 in which an electron injecting material is mixed with the electroluminescent material and co-deposited with it.
- 20 18. An electroluminescent device as claimed in claim 16 or 17 in which the electron injecting material is a metal complex or oxadiazole or an oxadiazole derivative.
19. An electroluminescent device as claimed in claim 18 in which the electron injecting material is an aluminium quinolate or 2-(4-biphenyl)-5-(4-tert-butylphenyl)-
- 25 1,3,4 oxadiazole.
20. An electroluminescent device as claimed in any one of claims 8 to 19 in which there is a dye incorporated in the electroluminescent layer.
- 30 21. An electroluminescent device as claimed in 20 in which the dye is a fluorescent

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laser dye or an electroluminescent laser dye.

22. An electroluminescent device as claimed in any one of the preceding claims 8 to 20 in which the anode is a metal.

5

23. An electroluminescent device as claimed in claim 22 in which the anode is a aluminium, magnesium, lithium, calcium or a magnesium silver alloy.

10 24. An electroluminescent device as claimed in any one of the preceding claims in which there are a plurality of layers of electroluminescent material.

25. An electroluminescent device as claimed in any one of the preceding claims in which the layer of electroluminescent material is formed of two or more different electroluminescent compounds.

15

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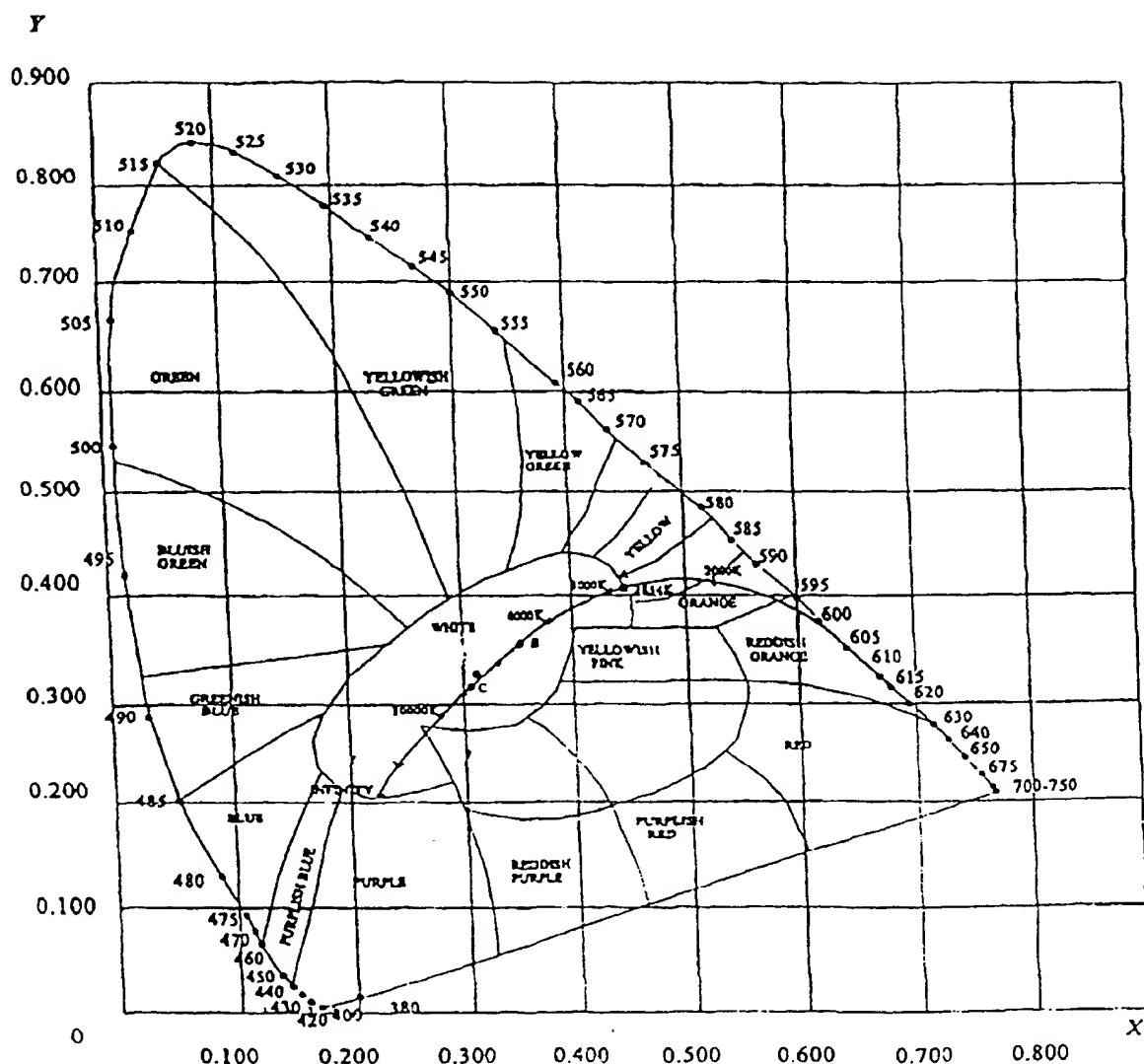


FIG. 1

CIE 1931 x,y chromaticity diagram showing approximate position of perceived colours

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## Example 1

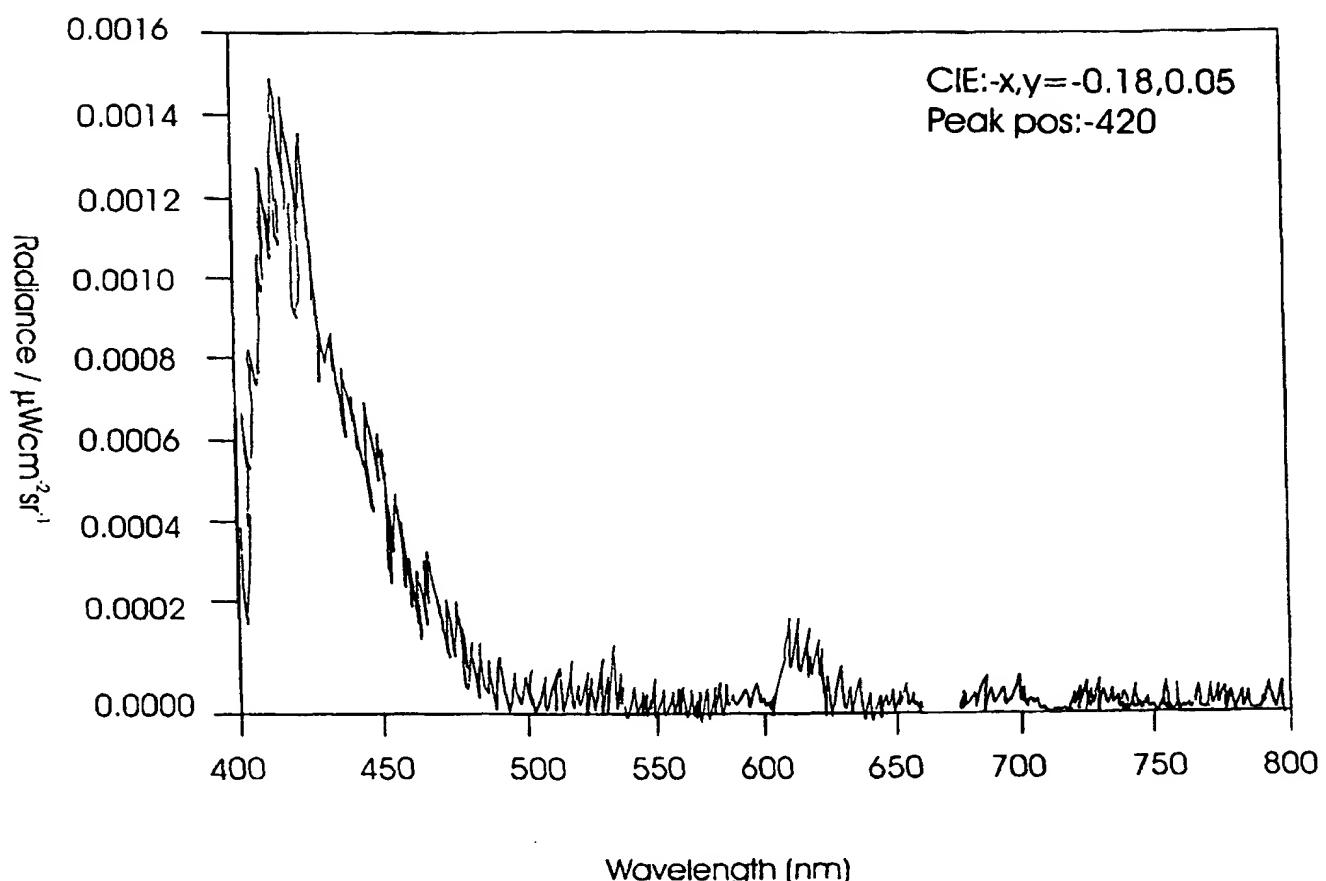


Fig. 2

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## Example 2

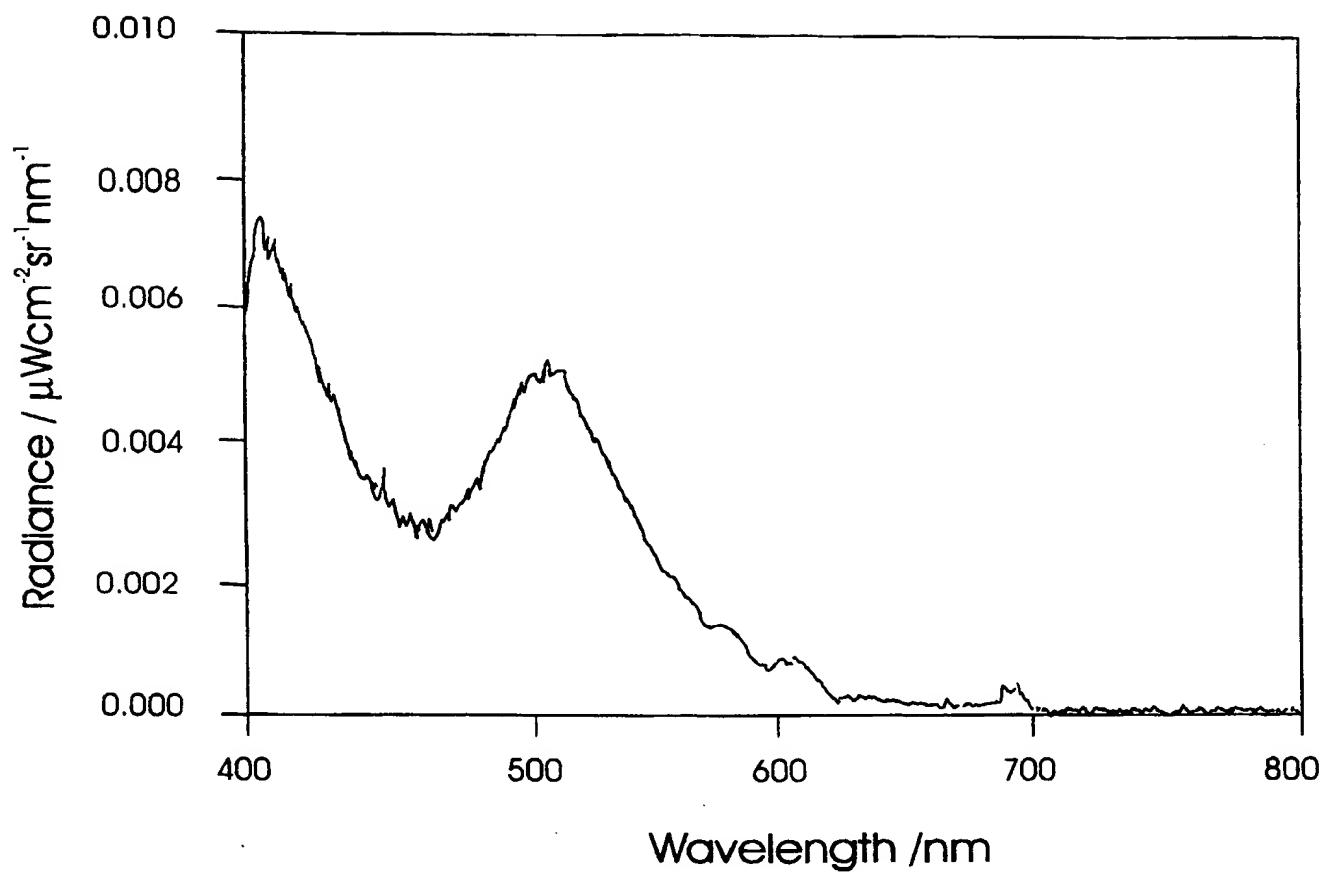


Fig. 3

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## Example 3

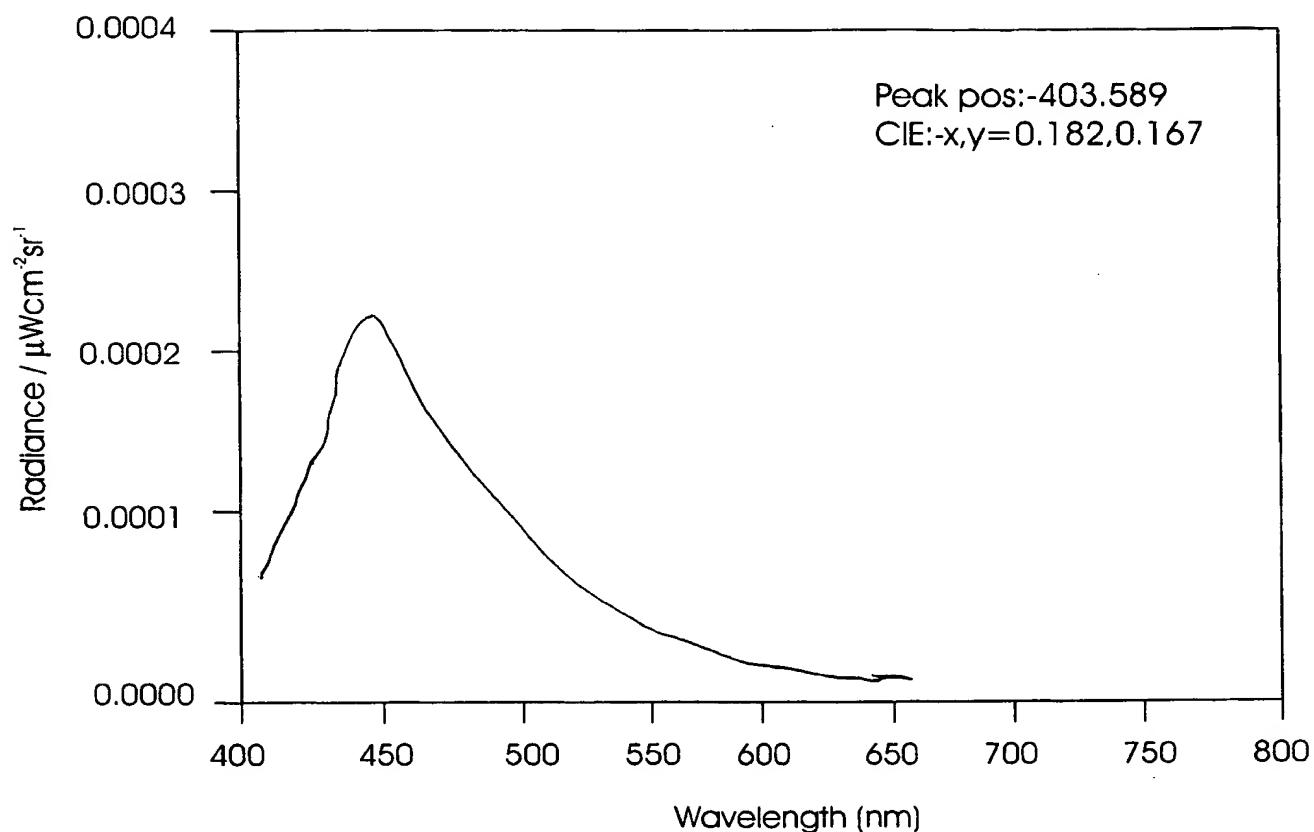


Fig. 4

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## Example 4

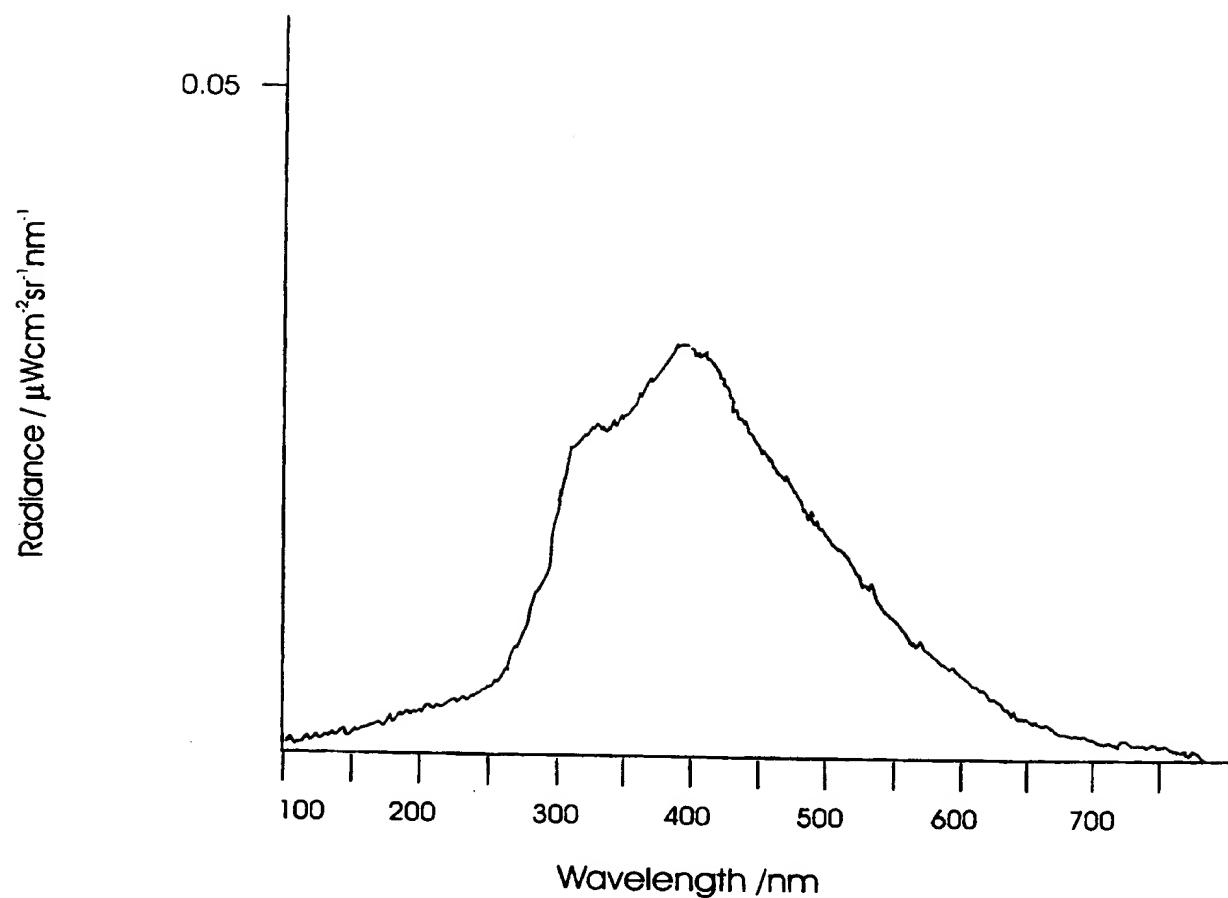


Fig. 5

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## Example 5

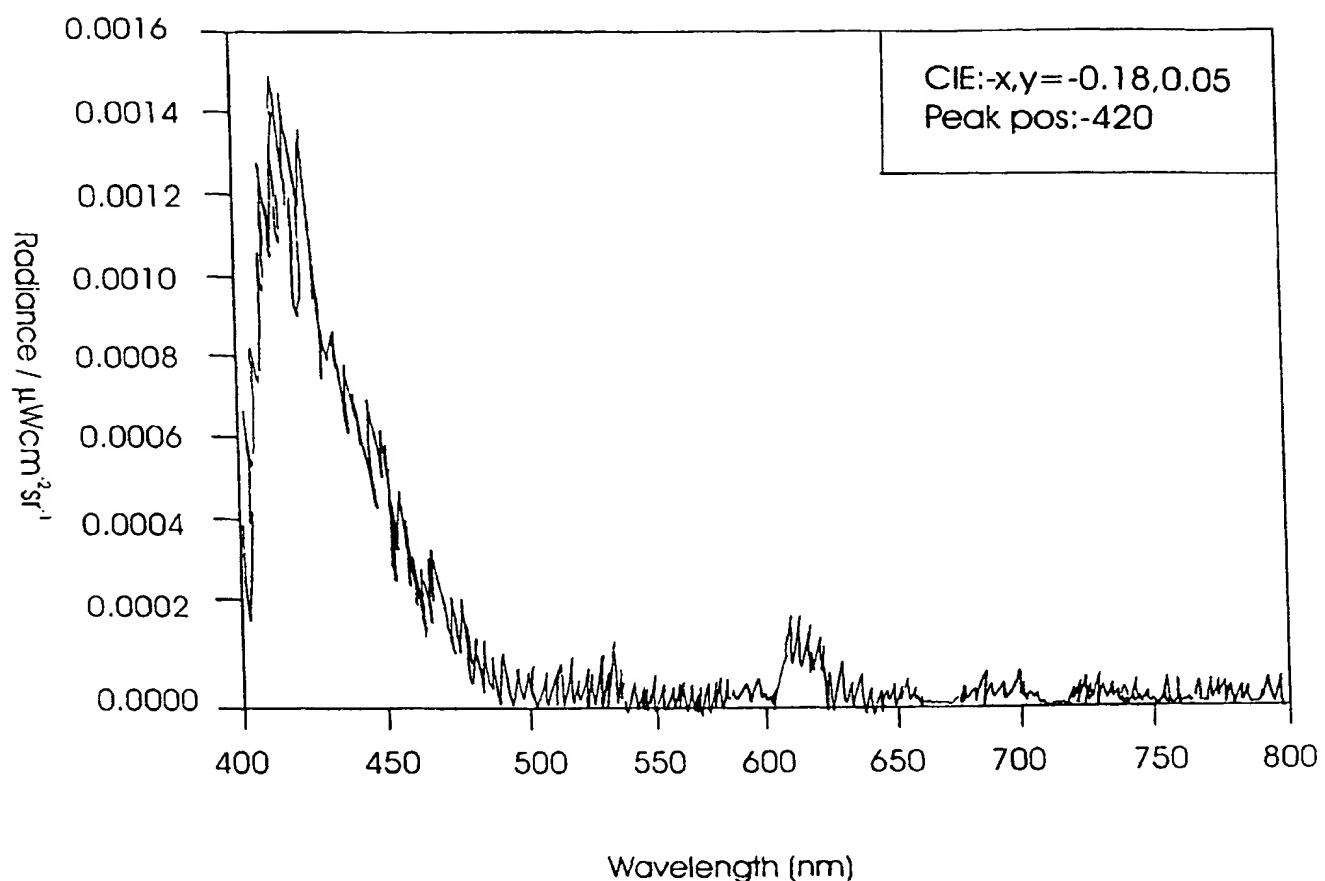


Fig. 6

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 99/03619A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09K11/06 H05B33/14 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09K H05B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International Application No
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International Application No

PCT/GB 99/03619

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